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(54) ORGANIC PRODUCTS AND LIQUID FUELS FROM
LIGNOCELLULOSIC MATERIALS BY VACUUM PYROLYSIS

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The present invention relates to the conversion of lignocellulosic material and peat into liquid organic components having a highly desirable commercial value either as fuel or as chemical feedstocks.

BACKGROUND OF THE INVENTION

There is a vast body of literature dealing with the conversion of coal and other carbonaceous materials to liquid and gaseous hydrocarbons and to clean solid fuel. Notwithstanding the vast amount of publications in this field, only a few commercial plants have been put into operation. With the ever increasing prices of crude oil, there is a renewed interest in finding and developing processes whereby dependance of crude oil by industrial countries will be decreased.

It will be readily appreciated that modern industrial chemistry depends largely on the by-products of crude oil, while modern transportation means directly depend on crude oil for its supplies of fuel. On the other hand, heating of residential and industrial buildings requires natural gas, heating oil or electricity, all of which are getting to be more and more expensive. On the other hand, there is a great availability of carbonaceous or lignocellulosic materials which when treated under certain conditions can provide various gaseous, liquid and solid organics.

In most prior art processes it has been noted that the pyrolysis procedure of carbonaceous material is carried out under conditions which go beyond the primary cracking stage whereby many of the valuable products obtained in the primary cracking stage are decomposed in the secondary cracking stage.

One such procedure has been described in USP 4,077,868, R.W. Chambers, inventor. In the procedure described in this U.S. patent, a carbonaceous material is moved through an elongated chamber maintained at a temperature of from 1000°F in the absence of oxygen and the



gases and vapors produced are withdrawn under reduced pressure within the tubular member whereby as they are withdrawn the gases and vapors formed are caused to travel through the carbonaceous material as it is moved through the tubular member. This system is such that a large proportion of hydrocarbon gases are formed rather than the highly desirable oils. The vacuum in the tube is moderate, being specified to vary from about 625 to 700 mm of mercury (absolute pressure), this range of vacuum being 10 specified so that the flow of gases and vapors through the carbonaceous mass is found to be fast enough to avoid re-polymerization, but not so fast as to prevent the formation of methane and the higher homologues of methane due to the reaction between hydrogen and carbon.

Essentially, the system just described is one which will convert about 10% of the original moisture-ash-free weight of the starting lignocellulosic material into combustible oils.

Accordingly, it would appear highly desirable to 20 provide a process for pyrolyzing lignocellulosic material to yield higher amounts of combustible oils.

DESCRIPTION OF THE INVENTION

Essentially, the present invention provides a method for pyrolyzing lignocellulosic materials whereby by avoiding or preventing secondary pyrolysis or cracking from taking place, there is obtained an unexpected higher yield of primary products than have been obtained by prior art processes.

The process of the present invention comprises 30 drying lignocellulosic materials to reduce moisture content and subjecting the dried peat to a temperature variation of from room temperature to a temperature within the range comprised between 350 and 950°C at a heating rate of at least 1°C/min., while maintaining the reaction zone under a vacuum of not more than 100 mm/Hg (absolute pressure) and recovering the decom-

posed materials as they are formed, thereby preventing same from undergoing further decomposition reactions, thus yielding mainly primary products. By proceeding in this manner, the decomposed materials are withdrawn from the reaction zone within approximately one second from their initial formation.

Most of the condensable organics are released before 530°C as it can be concluded from the examples given in the Tables where negligible differences exist 10 between the condensable organics obtained at 530°C and 950°C. Reactions beyond 530°C mainly produce more gas from the residual char.

It is also a feature of the present invention that catalysts may be incorporated in the starting lignocellulosic material by impregnation, deposition or simple addition, thereby to increase the yield and/or to modify the quality of the product distribution of the primary pyrolysis or cracking step.

As lignocellulosic materials which can be used 20 in accordance with the present invention, there may be mentioned peat, forest biomass, agricultural and vegetable materials such as wood blocks or chips, straw, corn stover and other similar materials. In order to maximize the thermal efficiency of the pyrolysis reactor and minimize its volume the lignocellulosic material should be partially dried so as to contain little moisture. Preferably the material is dried to about 10% moisture before been introduced in the reactor. In actual processing the drying step can be done separately or integrated in the overall 30 process implied by the present invention.

If desired, the lignocellulosic material can be impregnated with salt solutions of cobalt, nickel or iron or mixtures thereof. The amount of metal catalyst thus deposited can vary from 5 to 20 mg per gram of anhydrous lignocellulosic material. The addition of a metal catalyst results in a modification of both the yield and

the nature of the substances produced in the primary cracking.

The pyrolytic process of the present invention is carried out in a vertical cylindrical retort equipped with an appropriate internal liner. The retort is placed in a vertical three zone furnace equipped with an automatic temperature programmer for closely controlling the coking temperature up to 950°C if so desired. The temperature is adjusted so that it is raised at a rate of from 10°C/min. to 10°C/min. and is thus uniform throughout the whole section of the fixed bed.

The bottom of the retort is connected to a simple condensation system made up of two sections, one of which is refrigerated to a temperature of about 0°C, while the other is refrigerated to a temperature of about -78°C. As a precautionary measure, a porous glass wool plug is inserted between the last condensing unit and the vacuum pump to retain the last traces of light oils sucked by the vacuum pump.

As far as the non-condensable gases are concerned, they are collected in an appropriate container connected to the outlet of the vacuum pump and separated and analyzed by methods well known in the art.

The vacuum applied to the retort during the pyrolysis in accordance with the present invention should be smaller than 100 mm/Hg (absolute pressure). It has been found that by operating the pyrolysis in this manner, the products obtained by the initial or primary cracking are immediately removed from the reaction chamber before they can undergo a significant secondary cracking which is observed when operating at higher pressures. The net result is a substantially higher yield of condensable organic liquids such as tar and oils.

In other words, it has been unexpectedly found that by operating in vacuum as is done in the present invention, there is obtained a higher yield of condensable

organic liquids and a lower yield of char than is obtained when carrying the pyrolytic process under a lower vacuum or under atmospheric pressure.

In the present invention, the amount of condensable organic liquids has been found to vary from about 24 to 74% by weight of the treated m.a.f. carbonaceous feedstock, whereas the amount of char will vary from about 13 to 41% by weight of the treated m.a.f. mass and the non-condensable gases represent from about 10 to 27% by weight. The amount of each type of product recovered will vary depending on the lignocellulosic material used. A significant advantage of the process of the present invention is that the non-condensable gases obtained can be used to heat the chamber.

Another major feature of the present invention is that by simple impregnation of the original material with suitable catalysts, the yields of organic liquid products can be modified and considerably enhanced if the proper catalyst is used. For instance, poplar wood yields 51.2% weight of organic liquids when pyrolyzed in its raw state (at 10°C/min.) whereas the yield can be enhanced to 66.1% weight if small amounts of cobalt are added. The catalyst can be recovered into the unconverted solid residue (char).

The present invention will be more readily understood by referring to the following Examples which are given to illustrate the invention only.

EXAMPLE 1

60 g of red maple wood particles having a size of from 2.4 to 4.8 mm are charged into the homogeneous temperature zone of a closed reactor. The pressure inside the reactor is reduced to less than 1 torr. by means of a vacuum pump. The reactor is then heated at a rate of 10°C/min. up to 530°C. During this operation gases and vapors are released and condensed in appropriate traps. The non-condensable gases are pumped into a 20 l reservoir

for analysis. During the pyrolysis the total pressure in the reaction zone is maintained between 5 and 10 torr. The pyrolysis reaction is stopped once the release of gas is observed while keeping the reaction temperature at 530°C for 30 min. (pressure is observed to be less than 1 torr). At this point the reactor is switched off and the system is left to cool at room temperature.

Once the reactor at room temperature, argon is introduced in the entire system so that a slight positive 10 pressure (above atmospheric) is obtained. The system is then opened and the char recovered as well as the condensed tar.

The amounts of char and tar are determined by weighing in a calibrated scale. A xylol extraction permits the determination of the water present in the tar.

Once the gas composition is determined via G.C. analysis, the molecular weight of the produced gas is known and from the volume and total pressure the total amount of gas produced is calculated.

20 All the calculations are made on a moisture and ash free basis.

Results from this experiment are:

INPUT - m.a.f.	red maple :	60.0 g
OUTPUT - m.a.f.	char :	11.2 g
	oils :	29.0 g
	water :	12.8 g
	gases :	7.0 g

GAS COMPOSITION : (% vol.)

	H ₂	:	5.5
	CO	:	36.1
	CO ₂	:	42.7
	CH ₄	:	10.4
	C ₂ H ₄	:	0.6
	C ₂ H ₆	:	0.7
	C ₃ H ₆	:	0.2
	C ₃ H ₈	:	0.2
10	C ₄ H ₈	:	0.5
	C _n H _m	:	0.4

Average molecular weight of gas: 32.5 g/gmole

EXAMPLES 2-6

By proceeding in the same manner as described in Example 1 but impregnating the starting poplar with a solution of cobalt nitrate, nickel nitrate and ferrous nitrate so that the concentration of Co, Ni and Fe in the poplar is 10, 5.3 and 3.5 mg/g of poplar respectively. The results obtained are shown in Table 1. Examples 5 and 20 6 show the results obtained without any catalyst.

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Table 1 Examples of Yields following vacuum pyrolysis

Heating rate = $10^{\circ}\text{C}/\text{min.}$

Ex.	Wood Feedstock	Catalyst	Max. Temp. Reached ($^{\circ}\text{C}$)	Yields (% wt., m.a.f. feedstock)			
				Char.	Oils	Water	Gases
2	Poplar	Co	950	13.6	66.1	7.6	12.7
3	Poplar	Ni	950	14.3	60.2	13.7	11.8
4	Poplar	Fe	950	14.6	57.0	17.0	11.4
5	Poplar	None	950	15.4	51.2	19.7	13.7
6	Poplar	None	530	17.8	47.8	23.3	11.1

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EXAMPLES 7-13

Table 2 illustrates the results with different feedstocks at different temperatures by proceeding in accordance with Example 1.

Table 2 Examples of yields following vacuum pyrolysis
Heating rate = 10°C/min.

Ex.	Feedstock	Max. Temp. Reached (°C)	Yields (% wt., m.a.f. feedstock)				Gas Composition (% vol.)				
			Char	Oils	Water	Gases	H ₂	CO	CO ₂	CH ₄	Others
7	Maple Bark	530	16.7	31.0	27.3	25.0	7.8	25.1	49.7	13.0	4.4
8	Red Maple Wood	530	18.7	48.4	21.3	11.6	5.5	36.1	42.7	10.4	5.3
9	Oat Straw	930	19.9	31.9	22.1	26.1	27.9	29.8	21.4	11.9	9.0
10	Wheat Straw	530	20.5	38.9	25.2	15.4	0.0	34.6	52.8	8.7	3.9
11	Corn Stover	930	19.8	38.1	22.1	20.0	40.2	24.8	24.5	8.2	2.3
12	Peat	930	32.8	25.2	15.4	26.6	45.9	15.8	26.1	7.9	4.3
13	Peat	530	40.7	24.0	16.9	18.4	16.9	14.1	54.8	9.0	5.2

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for subjecting a lignocellulosic material to primary pyrolysis which comprises: introduction of air-dry lignocellulosic material into a reaction chamber where it is subjected to a temperature variation of from room temperature to a temperature within the range of from 350 to 950°C at a heating rate of from at least 1°C/min. while maintaining the reaction zone under a vacuum lower than 100 mm/Hg (absolute pressure) whereby as the primary thermal decomposition products are formed they are rapidly removed from the reaction zone thus yielding primary decomposition products containing at least 24% by weight of organic condensable products.
2. The process of Claim 1, wherein the initial lignocellulosic material is impregnated with a transition metal catalyst.
3. The process of Claim 1, wherein the lignocellulosic material is peat.
4. The process of Claim 1, wherein the lignocellulosic material is of agricultural nature.
5. The process of Claim 1, wherein the lignocellulosic material is wood and similar materials.
6. The process of Claim 1, wherein the amount of pyrolytic water is between 3 and 28% by weight, the amount of non-condensable gases is from 10 to 27% by weight, the amount of char is from 13 to 41% by weight and the amount of oils is from 24 to 74% by weight.



A B S T R A C T

A process is provided for subjecting a ligno-cellulosic material to primary pyrolysis which comprises: introduction of air-dry lignocellulosic material into a reaction chamber where it is subjected to a temperature variation of from room temperature to a temperature within the range of from 350 to 950°C at a heating rate of from at least 1°C/min. while maintaining the reaction zone under a vacuum lower than 100 mm/Hg (absolute pressure) whereby as the primary thermal decomposition products are formed they are rapidly removed from the reaction zone thus yielding primary decomposition products containing at least 24% by weight of organic condensable products.

SUBSTITUTE

REPLACEMENT

SECTION is not Present

Cette Section est Absente